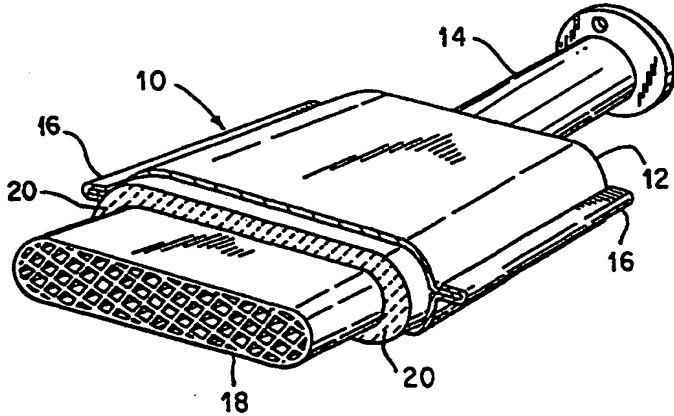


**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B01D 50/00, 53/34, F01N 3/10</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/46028</b> <b>(43) International Publication Date:</b> 16 September 1999 (16.09.99)
<b>(21) International Application Number:</b> PCT/US99/03461 <b>(22) International Filing Date:</b> 18 February 1999 (18.02.99)  <b>(30) Priority Data:</b> 09/038,243      11 March 1998 (11.03.98)      US  <b>(71) Applicant:</b> UNIFRAX CORPORATION [US/US]; 2351 Whirlpool Street, Niagara Falls, NY 14305-2413 (US).  <b>(72) Inventors:</b> FERNANDO, Joseph, A.; 4 Hummingbird Lane, Amherst, NY 14228 (US). TEN EYCK, John, D.; 1458 Ridge Road, Lewiston, NY 14092 (US). LACKI, Thomas, S.; 12327 South Blossom Lea, Alden, NY 14004 (US).  <b>(74) Agents:</b> CURATOLO, Joseph, G.; Renner, Kenner, Greive, Bobak, Taylor & Weber, Suite 280, 24500 Center Ridge Road, Westlake, OH 44145 (US) et al.		<b>(81) Designated States:</b> BR, CA, CN, IN, JP, KR, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SUPPORT ELEMENT FOR FRAGILE STRUCTURES SUCH AS CATALYTIC CONVERTERS    <b>(57) Abstract</b> <p>A support element (20) is disposed between a housing (12) and a fragile structure (18) resiliently mounted within the housing (12). The support element (20) includes an integral, substantially non-expanding ply or layer of melt-formed ceramic fibers containing at least alumina and silica. The fibers have an average diameter ranging from about 1 micron to about 14 microns and have been heat treated by treating the fibers at a temperature of at least 1100 °C over a 30-minute period, or at a temperature of at least 990 °C for a period of at least on hour. The resultant heat treated fibers exhibit suitable handling properties, have at least about 5 to about 50 percent crystallinity as detected by x-ray diffraction, and have a crystallite size of from about 50 Å to about 500 Å. The resultant support element (20) provides a minimum residual pressure for holding the fragile structure (18) within the housing (12) after 200 cycles of testing at 900 °C of at least 4 psi. Such a support element (20) may be used in devices for the treatment of exhaust gases, such as catalytic converters (10), diesel particulate traps and the like. A method of mounting a fragile structure (18) in such a device is also provided.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## **SUPPORT ELEMENT FOR FRAGILE STRUCTURES SUCH AS CATALYTIC CONVERTERS**

### **Field of the Invention**

5           The present invention is directed to catalytic converters, diesel particulate traps and other devices for the treatment of exhaust gases. More particularly, the present invention is directed to a device having a fragile structure mounted within a housing which is supported therein by a support element disposed between the housing and the fragile structure. The support element has improved resilience and handling properties as well as increased support pressure characteristics and comprises an integral, substantially  
10 nonexpanding ply or layer of melt-formed ceramic fibers for mounting and supporting the fragile structure. The improved characteristics of the non-intumescent support element are a result of controlled mullite microcrystal formation in the melt-formed ceramic fiber via heat treatments under a time-temperature regimen requiring the fiber be treated at  
15 temperatures of at least 1100°C for at least 30 minutes or at temperatures of at least 990°C for at least 1 hour.

### **Background of the Invention**

          Catalytic converter assemblies for treating exhaust gases of automotive and  
20 diesel engines contain a fragile structure, such as a catalyst support structure, for holding the catalyst, used to effect the oxidation of carbon monoxide and hydrocarbons and the reduction of oxides of nitrogen, the fragile structure being mounted within a metal housing. The fragile structure is preferably made of a frangible material, such as a monolithic structure formed of metal or a brittle, fireproof ceramic material such as  
25 aluminum oxide, silicon dioxide, magnesium oxide, zirconia, cordierite, silicon carbide and the like. These materials provide a skeleton type of structure with a plurality of tiny flow channels. However, as noted hereinabove, these structures can be, and oftentimes

are, very fragile. In fact, these monolithic structures can be so fragile that small shockloads or stresses are often sufficient to crack or crush them.

5 The fragile structure is contained within a metal housing, with a space or gap between the external surface of the fragile structure and the internal surface of the housing. In order to protect the fragile structure from thermal and mechanical shock and other stresses noted above, as well as to provide thermal insulation, it is known to position at least one ply or layer of mounting or support material within the gap between the fragile structure and the housing. For example, assignee's U.S. Patent Nos. 4,863,700,  
10 4,999,168, 5,032,441, and 5,580,532, the disclosure of each of which is incorporated herein by reference, disclose catalytic converter devices having a mounting or support material disposed within the gap between the housing and the fragile structure contained in the devices to protect the fragile structure and otherwise hold it in place within the housing.

15

However, even some of the latest mounting materials used in these catalytic converter devices, while suitable for most current automotive catalytic converters, do not entirely satisfy all design requirements of the fragile structure and catalytic converter manufacturers. In particular, the residual holding pressure exerted by many of the state-of-the-art plies of support material, often referred to as mounting mats, have been found  
20 to be inadequate at times where the catalytic converter has undergone wide temperature fluctuations, thereby causing significant expansion and contraction of the metal housing in relation to the fragile structure, also referred to as the catalyst support structure, which, in turn, causes significant compression and expansion cycles for the mounting mats over  
25 a period of time. It has been found that these state-of-the-art mounting mats do not sufficiently hold the fragile structure in the most severe of applications where temperatures

reach well above 900°C, and often undergo constant thermal cycling. Vibration and mechanical shock are further problems for the mounting mats.

These problems are even further amplified in catalytic converter systems having catalytic support structures greater than 35 mm in diameter because a larger structure implies a larger outer housing which, in turn, implies a larger gap expansion between the fragile support structure and housing at elevated temperatures due to the larger thermal expansion of the housing with respect to the fragile support structure. Under normal operating conditions, a minimum effective holding pressure for the support element or mat of approximately 2 psi is sufficient to prevent the fragile structure from being dislodged and damaged. The effective mat holding pressure is defined as the mat holding pressure multiplied by the coefficient of friction of the mat/fragile structure interface. The coefficient of friction of typical mat products is approximately 0.45 in the in-use condition. The mounting mat, therefore, is required to have a sufficient residual minimum holding pressure after 200 cycles of testing at a nominal temperature of 900°C of at least 4 psi, and after 1000 cycles of testing at a nominal temperature of 900°C of at least 4 psi. More preferably, the support element (*i.e.*, mounting mat) should have a minimum holding pressure after 200 cycles of testing at the nominal 900°C temperature of at least 10 psi. When tested after 1000 cycles at 900°C, the support mat should more preferably have a minimum holding pressure of at least 6 psi, and even more preferably, at least 12 psi. Still further, the support element should exhibit predictable and acceptable degradation with high temperature exposure and mechanical cycling, meaning the ply or plies should preferably exhibit a regular pattern of degradation of no more than about 1 psi per 100 cycles after about 600 cycles.

Most of the mounting mats, heretofore, have attempted to overcome the degradation and thermal cycling problems by using extremely expensive, high alumina

refractory ceramic fibers which add significantly to the cost of the production of the mounting mat. These refractory ceramic fibers are made from an aqueous solution or a colloidal dispersion that is called an "organosol" or a "sol gel". While ceramic fibers formed by sol gel processes may offer a high degree of resiliency needed for mounting  
5 monolithic structures, their high cost have forced manufacturers to seek other, less expensive solutions.

For instances, some manufacturers of mounting or support mats have resorted to expensive preprocessing such as stitch binding prior to installation of the mat.  
10 In other instances, the mounting material used may be required to be used in combination with other mounting materials, such as intumescent sheets and backing layers, in order to provide sufficient strength for handleability and for resiliency. These mounting materials are generally very thick and lack the structural integrity necessary, and may even require being handled in a bag to prevent crumbling. They are also difficult to cut to size for  
15 installation, and further must be compressed substantially to fit enough material needed for supportive mounting within the gap between the catalyst support structure and the housing. Consequently, "flashing" commonly occurs, with excess material being squeezed out of the housing.

20 As an alternative to using sol gel-derived, refractory ceramic fibers, attempts have been made to form the ceramic fibers using melt processing techniques. However, conventional melt-formed ceramic fibers typically contain shot, on the order of 30 to 60 percent, and have been deemed not suitable for the particular application of a mounting mat within a catalytic converter or other similar device. Although it is possible  
25 to treat the fibers to reduce the shot content to as low as 5 percent, at least some patents, such as U.S. Patent Nos. 4,929,429, 5,028,397 and 5,250,269, have suggested that these

treated fibers still lack the requisite resiliency and, therefore, are not capable of providing the necessary holding pressure at a nominal temperature of 900°C.

However, at least one patent has attempted to overcome these shortfalls with melt-formed refractory ceramic fibers. U.S. Patent No. 5,250,269 teaches that a mounting mat may have the requisite resiliency values if it is produced using a particular annealing process to form substantially amorphous refractory ceramic fibers for the mat. By "substantially amorphous" is meant that no crystallinity can be detected by x-ray diffraction. In order to obtain this result, U.S. Patent No. 5,250,269 specifies that annealing temperatures of at least 700°C and less than 990°C are required to achieve a substantially amorphous melt-formed ceramic fiber. It is suggested that the annealing process provides for suitable ceramic fibers having sufficient resiliency values, regardless of the amount of shot contained therein. The particular type of melt processed fibers employed, *i.e.*, melt blown fibers or melt spun fibers, is not disclosed in Patent No. 5,250,269.

In British Patent Specification No. 1,481,133, it is suggested that a blanket or sheet of amorphous ceramic fibers will retain a substantially permanent set under compression, but that good resiliency can be achieved by converting the fibers from an amorphous form to a fine-grained crystalline form having a crystalline size of less than 200Å, after which the blanket will return to about 85 to 90% of its original configuration after compression. This can be achieved, according to the British specification, by heating the fibers to a temperature above the devitrification temperature of about 950°C, while avoiding higher temperatures above about 1050°C, since higher temperatures are recognized as forming coarse-grained structures which, according to the British specification, produces poor handling properties. The fibers are heated at the above-noted temperatures for a period of time sufficient to produce devitrification throughout the

refractory ceramic fibers, but must be terminated prior to the onset of excessive grain growth. According to the British specification, such a time period may vary from 10 minutes to up to 1 hour.

5                   Although the British specification characterizes the fibers as capable of returning to at least 85 to 90 percent of its original configuration when a compression force is released, the specification does not specify what applications are suitable for such a blanker or sheet of fibers, although mats and blankets of refractory ceramic fibers were commonly used in the 1970's as furnace liners. There is no mention whatsoever of the  
10       fibers being suitable for use in the mounting mats of catalytic converters.

                  Nevertheless, the present invention seeks to use high index, crystallized, melt-formed ceramic fibers by heat treating them at temperatures above the mullite crystallization temperature of 980°C, and more preferably, at temperatures ranging from  
15       990°C to about 1400°C in a controlled manner to obtain specific amounts of crystallinity and crystallite size, thereby increasing fiber performance in the form of a catalytic converter support mat. Such fibers will desirably have at least about 5 to about 50 percent crystallinity as detected by x-ray diffraction, and a crystallite size of from about 50A to about 500A. When such fibers are employed, the support mat provides a  
20       minimum pressure for holding the fragile catalyst support structure within the housing after 200 cycles and/or after 1000°C of testing at 900°C of at least 4 psi.

#### Summary of the Invention

                  It is an object of the present invention to provide a device for the treatment  
25       of exhaust gases which includes a support element possessing improved holding pressure characteristics.



It is another object of the present invention to provide a device including a support element, as above, wherein the support element is formed from high index, melt-formed ceramic fibers of alumina and silica.

5           It is still another object of the present invention to provide a device including a substantially nonexpanding ply of melt-formed ceramic fibers, as above, wherein the ply is a result of controlled mullite microcrystal formation in the melt-formed ceramic fiber via heat treatment at temperatures ranging from at least 990°C to about 1400°C for 30 minutes or more, depending upon the heat treating temperature.

10

          It is yet another object of the present invention to provide a device including a support element exhibiting a sufficient holding pressure at a nominal temperature of 900°C of at least about 4 psi upon 200 cycles and/or 1000 cycles testing, and exhibiting predictable and acceptable degradation with high temperature exposure and  
15   mechanical cycling.

          At least one or more of the foregoing objects, together with the advantages thereof over the known art relating to catalytic converters and other devices for the treatment of exhaust gases, which shall become apparent from the specification which  
20   follows, are accomplished by the invention as hereinafter described and claimed.

          In general, the present invention provides, in combination with a housing and a fragile structure resiliently mounted within said housing, a support element disposed between the housing and the fragile structure and comprising an integral, substantially  
25   non-expanding ply of melt-formed ceramic fibers, the fibers containing at least alumina and silica, having an average diameter of from about 1 to about 14 microns, and having been heat treated under a time-temperature regimen of one of (i) heat treating the fibers

at a temperature of at least 1100°C for at least 30 minutes, and (ii) heat treating the fibers at a temperature of at least 990°C for at least one hour, such that the fibers exhibit suitable handling properties, have at least about 5 to about 50 percent crystallinity as detected by x-ray diffraction, and have a crystallite size of from about 50A to about 500A, and wherein the support element includes means for exerting a minimum pressure for holding the fragile structure within the housing after 200 cycles of testing at 900°C of at least 4 psi. Such a combination may be included within a number of different products, including devices for treatment of exhaust gases, catalytic converters and diesel particulate traps.

10

Other objects and aspects of the present invention may be achieved by a method for mounting a fragile structure having at least one inlet surface within a device having a housing to provide thermal insulation and mechanical shock resistance to the fragile structure, the method comprising the steps of: preparing a flexible support element comprising an integral, substantially non-expanding ply of melt-formed ceramic fibers containing at least alumina and silica, the fibers having an average diameter of from about 1 to about 14 microns, and having been heat treated under a time-temperature regimen of one of (i) heat treating the fibers at a temperature of at least 1100°C for at least 30 minutes, and (ii) heat treating the fibers at a temperature of at least 990°C for at least one hour before cooling the fibers such that the fibers exhibit suitable handling properties, have at least about 5 to about 50 percent crystallinity as detected by x-ray diffraction, and have a crystallite size of from about 50A to about 500A; wrapping the flexible support element around the entire perimeter of at least a portion of the structure's surfaces adjacent to the inlet face; forming a housing around the wrapped structure; and radially compressing the support element between the structure and the housing, wherein the support element includes means for exerting a minimum pressure for holding the fragile structure within the housing after 200 cycles of testing at 900°C of at least 4 psi.

20

25

Brief Description of the Drawings

Fig. 1 is a fragmentary, elevational view of a catalytic converter according to the present invention.

5                    Fig. 2 is a graphical representation of the minimum pressure exerted (i.e., load) in comparison to the number of cycles tested (i.e., up to 1000) for a number of support elements prepared in accordance with the present invention and compared to other mats and blankets of the prior art.

10                   Fig. 3 is a graphical representation of the maximum pressure exerted (i.e., load) in comparison to the number of cycles tested (i.e., up to 1000) for each of the support elements set forth in Fig. 2.

15                   Fig. 4 is a graphical representation of the percent mullite crystallinity of the ceramic fiber of the present invention as a function of the heat treatment temperature.

Fig. 5 is a graphical representation of the crystallite size of the ceramic fiber of the present invention as a function of the heat treatment temperature.

20                   Fig. 6 is a bar graph comparison of the volume loss (in cc) of support elements containing one of four tested fibers of the present invention or the prior art.

25                   Fig. 7 is a graphical representation of the minimum pressure exerted (i.e., load) in comparison to the number of cycles tested (i.e., up to 200) for a number of support elements prepared in accordance with the present invention and compared to other mats and blankets of the prior art.

### Detailed Description of the Invention

One representative form of a device for treating exhaust gases is shown as a catalytic converter, generally designated by the numeral 10 in Fig. 1. It will be understood that the present invention is not intended to be limited to use in the catalytic converter shown, and so the shape is shown only as an example to illustrate the invention. In fact, as noted hereinabove, the support element, or mounting mat as it is sometimes called, could be used to mount or support any fragile structure, such as a diesel particulate trap or the like. Nonautomotive applications for the support mat of the present invention include but are not limited to catalytic converters for chemical industry emission (exhaust) stacks. The term "fragile structure" is intended to mean and include structures such as metal or ceramic monoliths or the like which may be fragile or frangible in nature and would benefit from a support element such as is described herein.

Catalytic converter 10 includes a generally tubular housing 12 formed of two pieces of metal, e.g. high temperature-resistant steel. Housing 12 includes an inlet 14 at one end and an outlet (not shown) at its opposite end. The inlet 14 and outlet are suitably formed at their outer ends whereby they may be secured to conduits in the exhaust system of an internal combustion engine. Device 10 contains a fragile catalyst support structure, such as a frangible ceramic monolith 18 which is supported and restrained within housing 12 by a support element such as mat 20, to be further described. Monolith 18 includes a plurality of gas-pervious passages which extend axially from its inlet end surface at one end to its outlet end surface at its opposite end. Monolith 18 may be constructed of any suitable refractory metal or ceramic material in any known manner and configuration. Monoliths are typically oval or round in cross-sectional configuration, but other shapes are possible.

In accordance with the present invention, the monolith is spaced from its housing by a distance or a gap, which will vary according to the type and design of the device, e.g., a catalytic converter or a diesel particulate trap, utilized. This gap is filled with by a support element 20 to provide resilient support to the ceramic monolith 18. The  
5 resilient support element 20 provides both thermal insulation to the external environment and mechanical support to the catalyst support structure, protecting the fragile structure from mechanical shock. The support element 20 also possesses good handleability and is easily processed in the fabrication of devices utilizing its capabilities of maintaining a substantially stable and uniform minimum holding pressure of at least 4 psi after  
10 undergoing 200 or 1000 mechanical cycles at a nominal temperature of about 900°C and, more preferably, of maintaining a holding pressure of at least 6 psi, and even more preferably, at least 10 psi, after undergoing 200 cycles.

By the term "cycle" it is meant that the gap between the monolith (*i.e.*,  
15 fragile structure) and housing is opened and closed over a specific distance and at a predetermined rate. In order to simulate realistic conditions, the expansion of the gap between a housing and a fragile structure of 55 mm in diameter was determined by calculating the coefficient of thermal expansion of the conventional housing at a maximum temperature of 600°C. This calculation resulted in a gap expansion of 0.25 mm. Based  
20 upon this information, testing of the support element(s) was conducted by mounting a support element having a 2000 g/m<sup>2</sup> basis weight in an approximately 3.6 mm gap, thereby providing a compressed density of 0.55 g/cc at room temperature. The tested materials were then heat treated to 900°C at a rate of about 20°C per minute and held at that temperature throughout the test. The tested materials were then subjected to  
25 mechanical cycling, each "cycle" being defined over an approximately 28 second period of time wherein the 3.6 mm gap was opened 0.25 mm (10/1000th of an inch) and then closed 0.25 mm (10/1000th of an inch). After 200 or 1000 cycles, the

residual minimum holding pressure exerted by the support element was then determined as described previously. While certain prior art support elements may also have the capability of maintaining a "high" minimum pressure after 200 or 1000 cycles, those elements uniformly contain very expensive, sol gel derived, refractory ceramic fibers  
5 having a high alumina content of at least 70 percent, and oftentimes, higher.

In contrast, the support element 20 of the present invention comprises an integral, substantially non-expanding composite sheet of melt-formed refractory ceramic fibers of alumina and silica, and a binder. By "integral" it is meant that, after  
10 manufacture, the mounting mat has a self-supporting structure, needing no reinforcing or containment layers of fabric, plastic or paper, (including those which are stitch-bonded to the mat) and can be handled or manipulated without disintegration. By "substantially non-expanding" is meant that the ply does not readily expand upon the application of heat as would be expected with intumescent mats. Of course, some expansion of the ply does  
15 occur based upon its thermal coefficient of expansion. The amount of expansion, however, is very insubstantial as compared to the expansion of intumescent mats. It will be appreciated that the mounting mat is substantially devoid of intumescent materials and sol gel-derived ceramic fibers.

20 As noted hereinabove, the ceramic fibers which are useful in the support element of the present invention are melt-formed ceramic fibers containing alumina and silica, and more preferably, melt spun refractory ceramic fibers. More particularly, these fibers have been heat treated at temperatures ranging from at least 990°C to about 1400°C such that the fibers have at least about 5 to about 50 percent crystallinity as detected by  
25 x-ray diffraction, and a crystallite size of from about 50A to about 500A. The preferred fibers are those selected from the group consisting of aluminosilicates, and more preferably, include those aluminosilicate fibers having from about 40 to about 60 percent

alumina and from about 60 to about 40 percent silica, and more preferably, from about 47 to about 53 percent alumina and from about 47 to about 53 percent silica.

5 The fibers utilized in the plies of the present invention are melt-formed, preferably spun fibers of high purity chemically and preferably have an average diameter in the range of about 1 to about 10  $\mu\text{m}$ , and more preferably, in the range of about 3 to 6.5  $\mu\text{m}$ . The fibers are beneficiated as is well known in the art to obtain a greater than 90 percent fiber index, meaning they contain less than 10 percent shot, and preferably only about 5 percent shot.

10

It is important to note that the fibers of the present invention are further prepared by heat treating the fibers under one of two specific time-temperature regimens. In one case, the particular melt processing technique requires heat treating the fibers at a temperature of at least 1100°C for at least 30 minutes. Alternatively, the fibers may be heat treated at a lower temperature of at least 990°C, but must undergo this treatment for at least one hour. Thus, contrary to the British Patent Specification No. 1,481,133, the fibers of the present invention are either maintained at temperatures above the devitrification temperature, and more preferably, at least 100°C above the devitrification temperature of the fibers, or for a period of time well in excess of that suggested by the British patent reference. In any event, it has been found that such a treatment process provides melt-formed ceramic fibers suitable for the purposes of the present invention.

25 The fibers should preferably be heat treated at a temperature between 990°C and 1400°C. In a preferred embodiment, the heat treatment of the fibers involves treating the fibers at a temperature of at least 1100°C for at least two hours. It will be appreciated that the treatment time may be much longer, if desired, but improved fibers may or may not result from the longer heat treatment. For example, treatment of the fibers for an

entire day is possible, or even for an entire a week. While it is believed that longer treatment times might provide even higher holding pressures, the 30-minute/1 hour minimum time limits, and more preferably, the 2 hour time limit, has been deemed suitable for purposes of the present invention. Shorter times, however, are not.

5

Once the fibers have been crystallized to the parameters set forth above, they may then be formed into a support element. Typically a sacrificial binder is employed to bond initially the fibers together. The binders used in the present invention are typically organic binders. By "sacrificial" is meant that the binder will eventually be  
10 burned out of the mounting mat, leaving only the melt-formed ceramic fibers as the final support element.

Suitable binders include aqueous and nonaqueous binders, but preferably the binder utilized is a reactive, thermally setting latex which after cure is a flexible  
15 material that can be burned out of the installed mounting mat as indicated above. Examples of suitable binders or resins include, but are not limited to, aqueous based latexes of acrylics, styrene-butadiene, vinylpyridine, acrylonitrile, vinyl chloride, polyurethane and the like. Other resins include low temperature, flexible thermosetting resins such as unsaturated polyesters, epoxy resins and polyvinyl esters. Preferably, about  
20 5 to about 10 percent latex is employed, with about 8 percent being most preferred. Solvents for the binders can include water, or a suitable organic solvent, such as acetone, for the binder utilized. Solution strength of the binder in the solvent (if used) can be determined by conventional methods based on the binder loading desired and the workability of the binder system (viscosity, solids content, etc.)

25

The mounting mat or support element of the present invention can be prepared by any known techniques. For instance, using a papermaking process, ceramic



fibers are mixed with a binder to form a mixture or slurry. Any mixing means may be used, but preferably the fibrous components are mixed at about a 0.25% to 5% consistency or solids content (0.25-5 parts solids to 99.5-95 parts water). The slurry may then be diluted with water to enhance formation, and it may finally be flocculated with  
5 flocculating agent and drainage retention aid chemicals. Then, the flocculated mixture or slurry may be placed onto a papermaking machine to be formed into a ply of ceramic paper. Alternatively, the plies may be formed by vacuum casting the slurry. In either case, they are typically dried in ovens. For a more detailed description of the standard papermaking techniques employed, see U.S. Patent No. 3,458,329, the disclosure of which  
10 is incorporated herein by reference. This method typically breaks the fibers during processing. Accordingly the length of the fibers are generally about 0.025 cm to about 2.54 cm when this method is used.

Furthermore, the ceramic fibers may be processed into a mat or ply by  
15 conventional means such as dry air laying. The ply at this stage, has very little structural integrity and is very thick relative to the conventional catalytic converter and diesel trap mounting mats. The resultant mat can be dry needled, as is commonly known in the art, to densify the mat and increase its strength.

20 Where the dry air layering technique is used, the mat may be alternatively processed by the addition of a binder to the mat by impregnation to form a discontinuous fiber composite. In this technique, the binder is added after formation of the mat, rather than forming the mat prepreg as noted hereinabove with respect the conventional papermaking technique. This method of preparing the mat aids in maintaining fiber length  
25 by reducing breakage. Generally the length of the fibers are about 1 cm to about 10 cm, preferably about 1.25 cm to about 7.75 cm when this method is used.

Methods of impregnation of the mat with the binder include complete submersion of the mat in a liquid binder system, or alternatively spraying the mat. In a continuous procedure, a ceramic fiber mat which can be transported in roll form, is unwound and moved, such as on a conveyer or scrim, past spray nozzles which apply the binder to the mat. Alternatively, the mat can be gravity-fed past the spray nozzles. The mat/binder prepreg is then passed between press rolls which remove excess liquid and densify the prepreg to approximately its desired thickness.

The densified prepreg may then be passed through an oven to remove any remaining solvent and if necessary to partially cure the binder to form a composite. The drying and curing temperature is primarily dependent upon the binder and solvent (if any) used. The composite can then either be cut or rolled for storage or transportation.

The mounting mat can also be made in a batch mode, by immersing a section of the mat in a liquid binder, removing the prepreg and pressing to remove excess liquid, thereafter drying to form the composite and storing or cutting to size.

Regardless of which of the above-described techniques are employed, the composite can be cut, such as by die stamping, to form mounting mats of exact shapes and sizes with reproducible tolerances. This mounting mat exhibits suitable handling properties, meaning it can be easily handled and is not so brittle as to crumble in one's hand like many other blankets or mats. It can be easily and flexibly fitted around the catalyst support structure 18 without cracking and fabricated into the catalytic converter housing 12 to form a resilient support for the catalyst support structure 18, with minimal or no flashing such as by extrusion or flow of excess material into the flange 16 area and provides a holding pressure against the catalyst support structure 18 of at least 4 psi at a nominal temperature of 900°C after 200 cycles or 1000 cycles of gap expansion. More

preferably, the ply provides a minimum residual holding pressure against the catalyst support structure 18 of at least 10 psi at a nominal temperature of 900°C after 200 cycles, or at least 6 psi, and even more preferably, at least 12 psi, at 900°C after 1000 cycles.

5                   It will be appreciated that other fibers, such as E-glass, might also be added to the mounting mat composition in small quantities of 2 percent or less. Although studied have not been completed, it is believed that the E-glass has no benefit to the mat of the present invention, and may even cause it to degrade over a period of time.

10                   In operation, the catalytic converter experiences a significant change in temperature. Due to the differences in their thermal expansion coefficients, the housing 12 may expand more than the support structure 18, such that the gap between these elements will increase slightly. In a typical case, the gap may expand and contract on the order of 0.25 mm during thermal cycling of the converter. The thickness and mounting  
15 density of the mounting mat is selected such that a minimum holding pressure of at least 4 psi is maintained under all conditions to prevent the fragile structure from vibrating loose. The substantially stable mounting pressure exerted by the mounting mat 20 under these conditions permits accommodation of the thermal characteristics of the assembly without compromising the physical integrity of the constituent elements.

20

                  Having describe the invention in general terms, it is now illustrated in greater detail by way of examples. It will be understood that these examples are for illustration only and should not be considered limiting in any respect, unless otherwise stated. These examples are used to demonstrate practice of the invention only.

25

                  Initially, melt-formed ceramic fibers of high purity chemistry comprising from about 47 percent to about 53 percent alumina and from about 47 percent to about

53 percent silica were prepared. The fibers had a mean diameter in the range of from about 5.4  $\mu\text{m}$  to about 6.2  $\mu\text{m}$ . The fibers were washed in a conventional manner to obtain a greater than 90 percent fiber index and thereafter were heat treated at a temperature between at least 990°C and about 1400°C. More particularly, most of these  
5 examples were heat treated at a temperature between about 1100°C and 1150°C. The particular heat treatment schedule involved a 1 hour ramp time and a 2 hour soak time at the target temperature about between 1100°C and 1150°C. The heat treated fibers were then incorporated into mat form via a conventional papermaking process using about 8 percent latex binder. In some instances, up to about 2 percent E-glass may also have been  
10 added to the ply of fibers, but these E-glass fibers are not believed to have affected the essential nature of the invention.

In order to demonstrate practice of the invention, five sample mats, prepared according to the concepts of the present invention (Examples 1-5), and  
15 comprising fibers as shown in Table I, were prepared, and tested to determine their minimum residual holding pressure. The mats had a 2000  $\text{g/m}^2$  basis weight and were mounted in a 3.6 mm gap, giving a compressed density of about 0.55  $\text{g/cc}$  at room temperature. The mats were then heated to 900°C and the temperature remained there for the duration of the test. The gap was then opened 10/1000ths of an inch (0.25 mm) and  
20 then closed 10/1000ths of an inch (0.25 mm) over the course of about 28 seconds, to delineate one cycle. The mats were tested at a constant temperature of about 900°C for 200 and 1000 cycles, respectively. The minimum resulting holding pressure for each mat was recorded and is set forth in Table I. The results of these tests were then compared to the results of the same tests with respect to competitive mats prepared from 100%  
25 mullite sol-gel fiber (Example A) and from a mixture of about 75 percent sol gel ceramic fiber and about 25 percent amorphous aluminosilicate fiber (Example B). Other mats were prepared based upon the disclosure of British Patent Specification No. 1,481,133,

including a high purity, melt-blown, small diameter aluminosilicate fiber (Example C) and a larger diameter, Kaolin-based fiber (Example D). The comparison is shown in Table I.

TABLE I

Sample Fiber Compositions and Resultant P min (at 900°C) after 200 and 1000 Cycles of Compression, Respectively

Example No.	Fiber Description	Target Temp. (°C)	Time	P min at 200 cycles at 900°C (psi)	P min at 1000 cycles at 900°C (psi)
1	98% melt spun large diameter aluminosilicate fiber; 2% E-glass	1300°C	2 hour	13.13	9.22
2	98% melt spun small diameter aluminosilicate fiber; 2% E-glass	1100°C	2 hour	--	6.81
3	98% melt spun large diameter aluminosilicate fiber; 2% E-glass	1100°C	2 hour	19.03	10.0
A	100% sol-gel mullite fiber	--	--	16.24	12.46
B	75% sol-gel fiber; 25% amorphous aluminosilicate fiber	--	--	3.59	1.55
C	100% melt blown small diameter aluminosilicate fiber	1050°C	30 minutes	0.88	--
D	100% Kaolin-based fiber	1050°C	1 hour	0.86	--

TABLE I Cont.

Sample Fiber Compositions and Resultant P min (at 900°C) after 200 and 1000 Cycles of Compression, Respectively

Example No.	Fiber Description	Target Temp. (°C)	Time	P min at 200 cycles at 900°C (psi)	P min at 1000 cycles at 900°C (psi)
4	100% melt spun large diameter aluminosilicate fiber	1100°C	2 hours	14.37	8.16
5	100% melt spun large diameter aluminosilicate fiber	1200°C	2 hours	18.22	10.26

5           The most important comparisons to be made from the Table I are with respect to the data showing the performance of the ceramic fiber mats for the minimum holding pressure or load ( $P_{min}$ ) after the 200th and 1000th cycle in the test. It will be appreciated that while the very expensive 100% mullite fiber showed the best results of about 12.46 psi after 1000 cycles, the minimum pressures exerted by all of the mats of  
10 the present invention were above at least 6 psi, after 1000 cycles. Moreover, of the mats of the present invention which were tested after 200 cycles, each mat maintained a minimum pressure of at least 13 psi at 900°C.

          With respect to further data, Figures 2 and 3 show various data point which  
15 show a recognizable and predictable pattern for the minimum and maximum pressures over the complete 1000 cycles of the compression test at 900°C. The fact that the tested mats exhibit predictable behavior with respect to degradation due to high temperature exposure and mechanical cycling makes them further useful.

20           Figures 4 and 5 illustrate the percent crystallinity and crystallite size data for the fibers used in the present invention. Based upon this data, the present invention specifies a percent crystallinity of between about 5 percent and about 50 percent by weight, while crystallite size ranges from about 50A to about 500A. From the data in Fig. 5, it will be appreciated that fibers having a crystallite size larger than 200A does not  
25 hinder the present invention, contrary to the statements found in the British Patent Specification No. 1,481,133. In fact, it will be appreciated that larger or smaller size particles may or may not be useful to the present invention.

          Figure 6 illustrates the comparative durability performance of the mats. It  
30 should be noted that the volume loss in all of the samples tested is relatively negligible and that the seemingly large difference between the results is basically insignificant. Any



product with less than 0.3 cc volume loss would be considered to have adequate durability.

Finally, Figure 7 illustrates the recognizable and predictable pattern for the minimum holding pressures over 200 cycles of the compression test at 900°C for other samples of material. In particular, Samples 4 and 5 contain melt-spun, large diameter fibers of aluminosilicate. The samples were heated to 1100°C and 1200°C, respectively, for 2 hours. In contrast, it will be appreciated that Sample C contains high purity, high index aluminosilicate fibers having average diameters of between about 1.5 and 2.5 microns. This sample was heat treated to 1050°C for 30 minutes as set forth in the British Patent Specification No. 1,481,133. Similarly, Sample D used Kaolin-based, high index fibers having an average diameter of about 3 microns. That sample was heat treated to 1050°C for 1 hour, and still did not maintain a residual minimum pressure upon testing at 900°C after 200 cycles of at least 4 psi. The samples of the present invention, on the other hand, were consistently above 4 psi.

In light of the excellent physical property characteristics demonstrated by the mounting mats/support elements of the present invention, these mats are believed desirable to at least the catalytic converter and diesel trap designers and manufacturers. The mounting mats can be die cut and are operable as resilient supports in a thin profile, providing ease of handling, and in a flexible form, so as to be able to provide a total wrap of the catalyst support structure without cracking. Alternatively, the mounting mat may be integrally wrapped about the entire circumference or perimeter of at least a portion of the catalyst support structure. The mounting mat may also be partially wrapped and include an end-seal as currently used in some conventional converter devices, if desired, to prevent gas by-pass.

The present invention is useful in a variety of applications such as catalytic converters for, *inter alia*, motorcycles and other small engine machines, and automotive preconverters, as well as high temperature spacers, gaskets, and even future generation automotive underbody catalytic converter systems. Generally, the present invention can  
5 be used in any application requiring a mat or gasket to exert holding pressure at room temperature and, more importantly, to provide the ability to maintain the holding pressure at elevated temperatures of from about 20°C to about 1300°C and during thermal cycling.

The mounting mat of the present invention can also be used in catalytic  
10 converters employed in the chemical industry which are located within exhaust or emission stacks, and which also contain fragile honeycomb type structures to be protectively mounted.

Thus, the objects of the invention are accomplished by the present  
15 invention, which is not limited to the specific embodiments described above, but which includes variations, modifications and equivalent embodiments defined by the following claims.

We claim:

- 1 1. In combination with a housing and a fragile structure resiliently mounted within  
2 said housing, a support element disposed between the housing and the fragile  
3 structure and comprising an integral, substantially non-expanding ply of melt-  
4 formed ceramic fibers containing alumina and silica, said fibers having an average  
5 diameter of from about 1 micron to about 14 microns and having been heat treated  
6 under a time-temperature regimen of one of (i) heat treating said fibers at a  
7 temperature of at least 1100°C for at least 30 minutes, and (ii) heat treating said  
8 fibers at a temperature of at least 990°C for at least one hour, such that the fibers  
9 exhibit suitable handling properties, have at least about 5 to about 50 percent  
10 crystallinity as detected by x-ray diffraction, and have a crystallite size of from  
11 about 50Å to about 500Å; and wherein the support element includes means for  
12 exerting a minimum residual pressure for holding the fragile structure within the  
13 housing after 200 cycles of testing at 900°C of at least 4 psi.
- 1 2. The combination as set forth in claim 1 wherein the fragile structure has a  
2 perimeter, at least a portion of which is integrally wrapped by the support element.
- 1 3. The combination as set forth in claim 1 wherein the fibers are selected from the  
2 group consisting of aluminosilicates.
- 1 4. The combination as set forth in claim 3 wherein the fibers are aluminosilicate  
2 comprising about 40 weight percent to about 60 weight percent alumina and about  
3 60 weight percent to about 40 weight percent silica.
- 1 5. The combination as set forth in claim 1 wherein the fibers have average diameters  
2 ranging from about 3 microns to about 6.5 microns.

- 1 6. The combination as set forth in claim 1 wherein the fibers have less than about  
2 10% shot.
- 1 7. The combination as set forth in claim 1 wherein the fibers are heated treated by  
2 maintaining the fibers at a temperature between 1100°C and about 1400°C for at  
3 least one hour.
- 1 8. The combination as set forth in claim 1 wherein the support element provides a  
2 minimum residual pressure for holding the fragile structure within the housing  
3 after 200 cycles of testing at 900°C of at least 10 psi.
- 1 9. The combination as set forth in claim 1 wherein the support element is prepared  
2 by the process comprising melt spinning the fibers; heat treating the fibers; and  
3 incorporating the fibers into mat form.
- 1 10. The combination as set forth in claim 1 wherein the fibers have been heat treated  
2 under a time-temperature regimen of heat treating the fibers at a temperature of  
3 at least about 1100°C for at least two hours.
- 1 11. A device for the treatment of exhaust gases comprising the combination set forth  
2 in any of claims 1 to 10.
- 1 12. A catalytic converter comprising the combination set forth in any of claims 1  
2 to 10.
- 1 13. A diesel particulate trap comprising the combination set forth in any of claims 1  
2 to 10.

- 1 14. A method for mounting a fragile structure having at least one inlet surface within  
2 a device having a housing to provide thermal insulation and mechanical shock  
3 resistance to the fragile structure, the method comprising the steps of:  
4 preparing a flexible support element comprising an integral, substantially  
5 non-expanding ply of melt-formed ceramic fibers containing alumina and silica,  
6 said fibers having an average diameter of from about 1 micron to about 14  
7 microns, and having been heat treated under a time-temperature regimen of one  
8 of (i) heat treating the fibers at a temperature of at least 1100°C for at least 30  
9 minutes, and (ii) heat treating the fibers at a temperature of at least 990°C for at  
10 least one hour before cooling the fibers such that the fibers exhibit suitable  
11 handling properties, have at least about 5 to about 50 percent crystallinity as  
12 detected by x-ray diffraction, and have a crystallite size of from about 50A to  
13 about 500A;  
14 wrapping the flexible support element around the entire perimeter of at  
15 least a portion of the structure's surfaces adjacent to the inlet face, and  
16 forming a housing around the wrapped structure, and  
17 radially compressing said support element between said structure and said  
18 housing,  
19 wherein said support element includes means for exerting a minimum  
20 residual pressure for holding the fragile structure within the housing after 200  
21 cycles of testing at 900°C of at least 4 psi.
- 1 15. The method as set forth in claim 14, wherein said ply has an uninstalled nominal  
2 thickness of about 3 mm to about 30 mm, an uninstalled nominal density of about  
3 0.03 to about 0.3 grams per cubic centimeter, and an installed thickness of about  
4 2 mm to about 8 mm.

- 1 16. The method as set forth in claim 14, wherein the flexible support element is  
2 further prepared by impregnation of said ply of said melt-formed ceramic fibers  
3 with a binder.
- 1 17. A method as set forth in claim 14, wherein the step of preparing includes heat  
2 treating the fibers at a temperature of at least 1100°C for at least two hours.

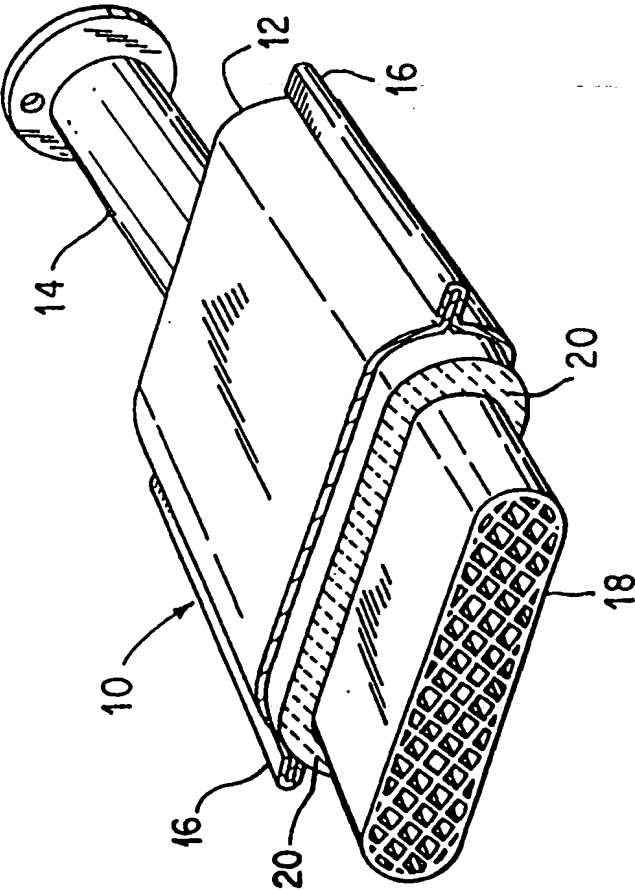
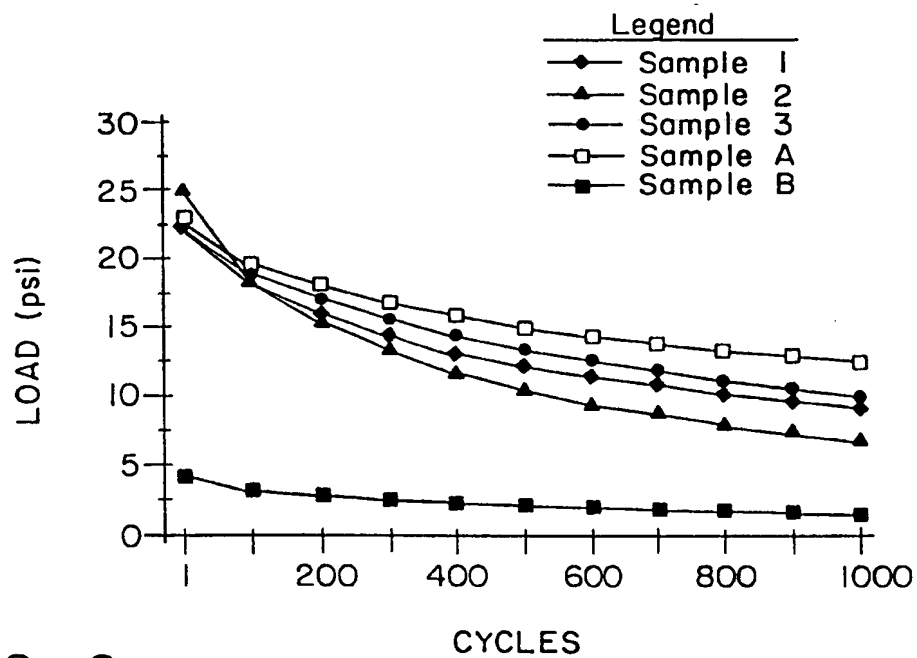
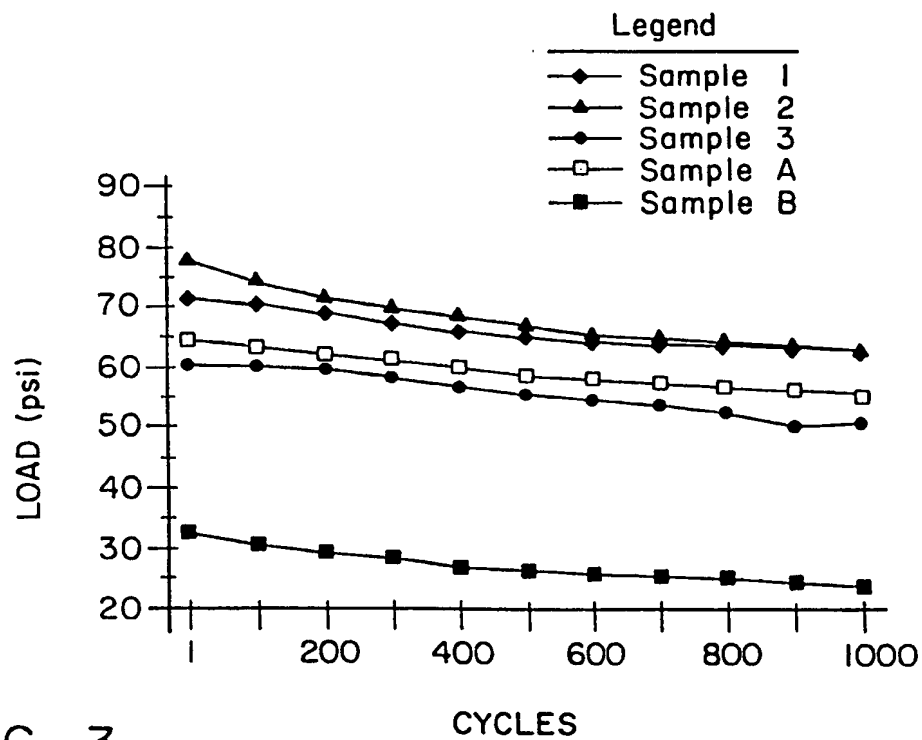


FIG. 1

2/6

FIG.-2FIG.-3



3/6

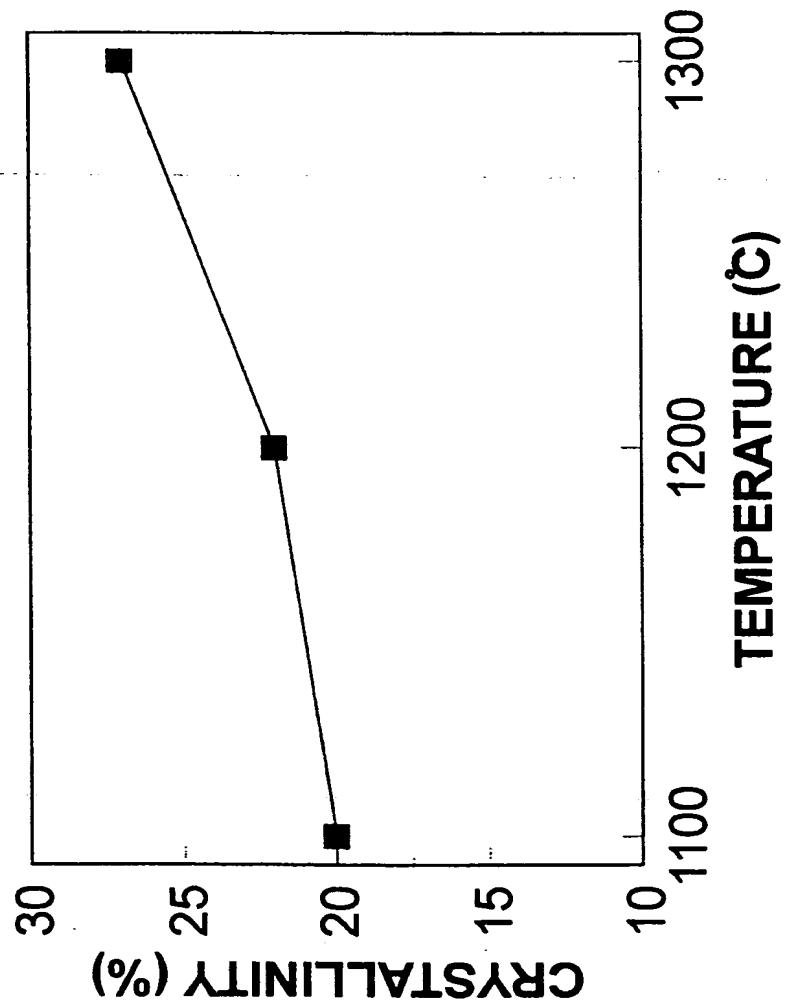
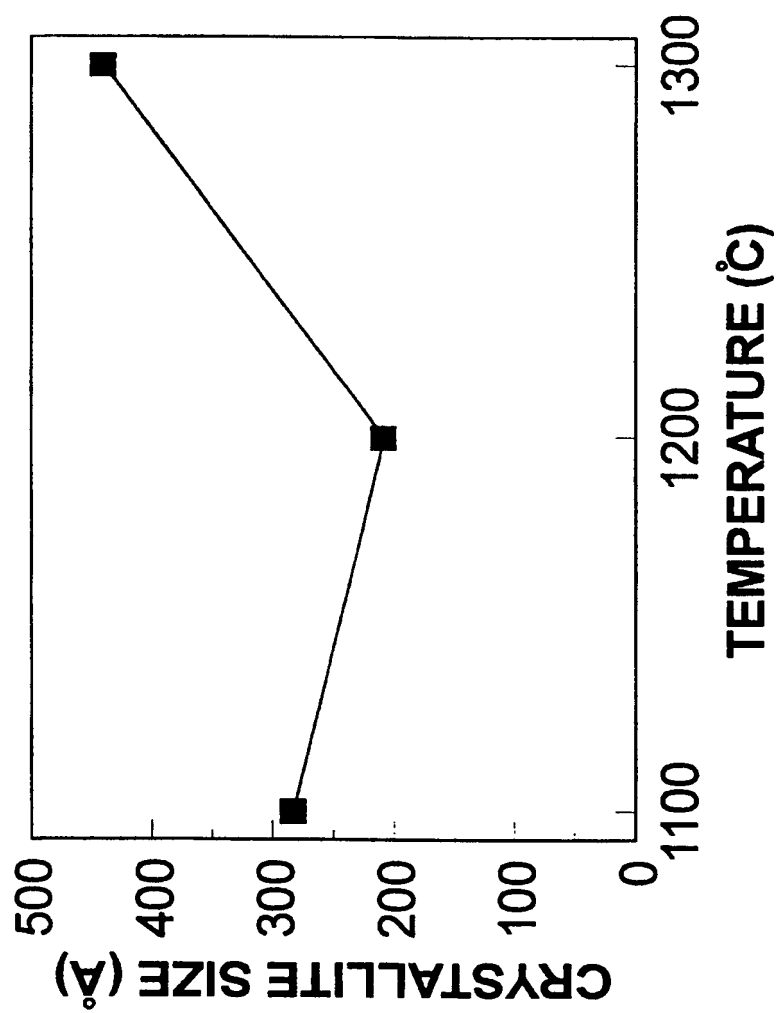
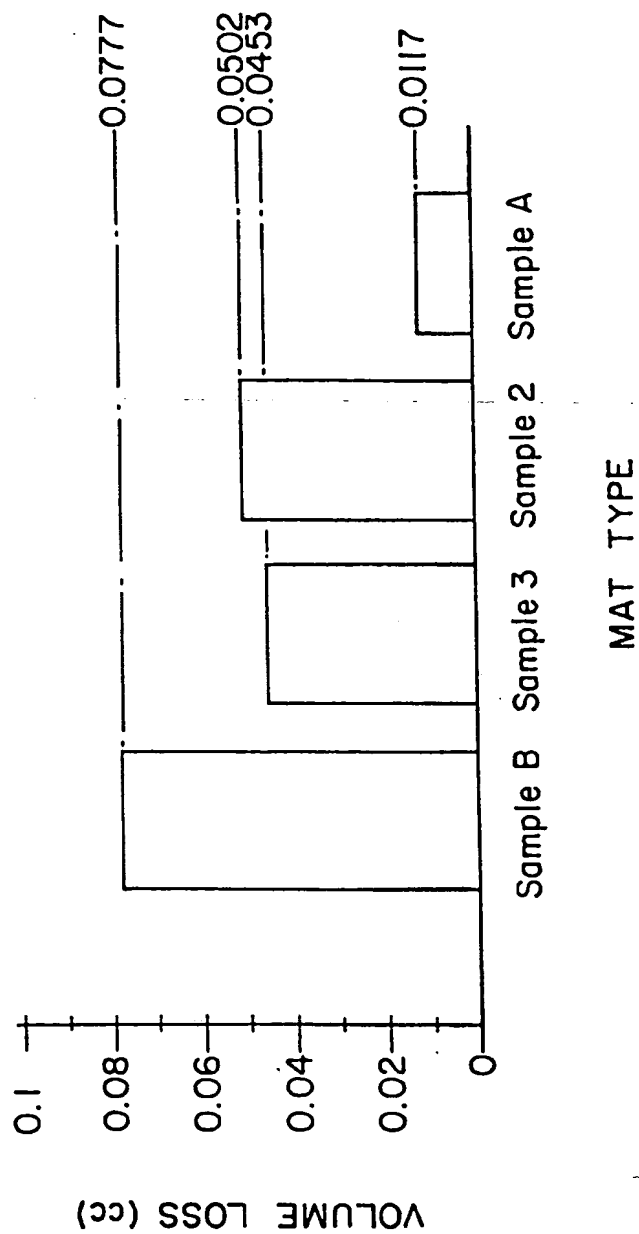


FIG.-4

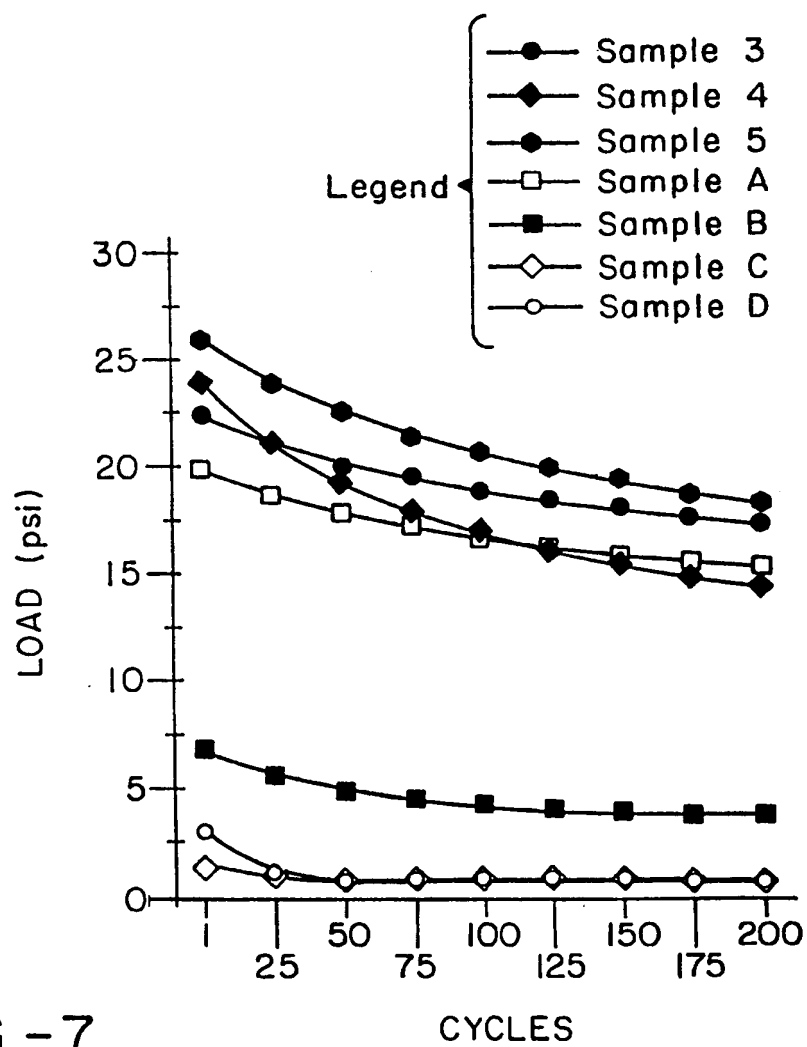
4/6

FIG.- 5

5/6

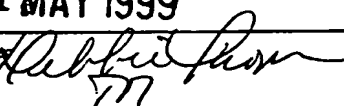
FIG.-6

6/6

FIG.-7

## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US99/03461

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) : B01D 50/00, 53/34; F01N 3/10 US CL : 422/179, 180, 221, 222; 428/920; 501/95.01, 95.02; 55/523 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 422/179, 180, 221, 222; 428/920, 921; 501/95.01, 95.02; 55/523, dig. 30 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS search terms: ceramic fibers, non-expand, catalyst		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 1,481,133 A (JOHNSON ET AL) 27 July 1977, see entire document.	1-17
Y	US 5,580,532 A (ROBINSON ET AL) 03 December 1996, see entire document.	1-17
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *B* earlier document published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *A* document member of the same patent family		
Date of the actual completion of the international search 23 APRIL 1999		Date of mailing of the international search report 11 MAY 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer  HIEN TRAN Telephone No. (703) 308-0661



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B01D 50/00, 53/34, F01N 3/10</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/46028</b> <b>(43) International Publication Date:</b> 16 September 1999 (16.09.99)
<b>(21) International Application Number:</b> PCT/US99/03461 <b>(22) International Filing Date:</b> 18 February 1999 (18.02.99)  <b>(30) Priority Data:</b> 09/038,243      11 March 1998 (11.03.98)      US  <b>(71) Applicant:</b> UNIFRAX CORPORATION [US/US]; 2351 Whirlpool Street, Niagara Falls, NY 14305-2413 (US).  <b>(72) Inventors:</b> FERNANDO, Joseph, A.; 4 Hummingbird Lane, Amherst, NY 14228 (US). TEN EYCK, John, D.; 1458 Ridge Road, Lewiston, NY 14092 (US). LACKI, Thomas, S.; 12327 South Blossom Lea, Alden, NY 14004 (US).  <b>(74) Agents:</b> CURATOLO, Joseph, G.; Renner, Kenner, Greive, Bobak, Taylor & Weber, Suite 280, 24500 Center Ridge Road, Westlake, OH 44145 (US) et al.		<b>(81) Designated States:</b> AU, BR, CA, CN, IN, JP, KR, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SUPPORT ELEMENT FOR FRAGILE STRUCTURES SUCH AS CATALYTIC CONVERTERS		
<div style="text-align: center;"> </div>		
<b>(57) Abstract</b> <p>A support element (20) is disposed between a housing (12) and a fragile structure (18) resiliently mounted within the housing (12). The support element (20) includes an integral, substantially non-expanding ply or layer of melt-formed ceramic fibers containing at least alumina and silica. The fibers have an average diameter ranging from about 1 micron to about 14 microns and have been heat treated by treating the fibers at a temperature of at least 1100 °C over a 30-minute period, or at a temperature of at least 990 °C for a period of at least one hour. The resultant heat treated fibers exhibit suitable handling properties, have at least about 5 to about 50 percent crystallinity as detected by x-ray diffraction, and have a crystallite size of from about 50 Å to about 500 Å. The resultant support element (20) provides a minimum residual pressure for holding the fragile structure (18) within the housing (12) after 200 cycles of testing at 900 °C of at least 4 psi. Such a support element (20) may be used in devices for the treatment of exhaust gases, such as catalytic converters (10), diesel particulate traps and the like. A method of mounting a fragile structure (18) in such a device is also provided.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**THIS PAGE BLANK (USPTO)**